Chemical Bath Deposition of Amorphous Indium Selenide Films from Alkaline Bath useful for Solar Cell Application

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 Abstract:- This paper presents the deposition and characterization of the Indium selenide (In2Se3) films onto the non-conducting glass and conducting indium tin oxide coated glass substrates in alkaline bath using chemical solution technique, respectively. The films were deposited by using Indium sulfate and selenium powder as precursors of In3+ and Se2- species at room temperature for deposition time of 46 h, respectively. The structural, surface morphological and optical properties of the deposited films were studied to decide the suitability of the deposited materials for various applications including photovoltaic. X-ray diffraction studies revealed that amorphous nature of the deposited films. The scanning electron microscopy showed formation of clusters with well defined boundaries. Optical absorption study showed the band gap of about 1.5 eV for the deposited film, suggesting In2Se3, a suitable candidate as an absorber in photoelectron chemical solar cell applications.
Keywords: Indium selenide, chemical bath deposition, thin films.

I.   INTRODUCTION

Amorphous semiconductors are attracting the researchers now a days because of their low cost that of crystal semiconductors. Indium (III) selenide is III–VI semiconductor with a direct band gap of 1.4 to 1.7 eV [1, 2], existing in three different phases α, β and γ [2, 3]. The band gaps of III–VI layered semiconductors like In2Se3 are generally narrow at room temperature, which makes them attractive for solar energy conversion and optoelectronic devices [4, 5] and therefore, have potential in solar energy conversion applications [6]. Structurally, In2Se3 comprises primitive layers of four atomic planes, Se–In–In–Se; the selenium atoms form two-dimensional hexagonally close-packed sheets, which provide the crystal with the hexagonal structure[7].The two most common forms of crystalline In2Se3 are the α (layered structure) andγ (the 'defect wurtzite structure') [8].Other commonly known forms include the b and d phases [9],as well as the recently discovered k phase(anisotropic structure) [10].The potential application of γ-In2Se3 as an absorber material for photovoltaic devices has resulted strong interest in the study of these films due to suitable optical and electrical properties [11].It exhibits at least three different crystalline modifications denoted by α, β and γ with a transition temperature of 200 and 650 °C , respectively, for the β-γ and α-β transitions[12].Un-doped In2Se3 is a n-type semiconductor in the form of hexagonal structure with a direct band gap of 1.7 eV[13].

Depending on the synthetic technique and reaction conditions, one of the crystalline forms of indium (III) selenide is produced, each form having a unique range of structural and electronic properties. Various atomic arrangements of indium (III) selenide materials have been reported in the literature: microporous (framework) materials of high structural complexity [12, 13], open frame work chalcogenides, noncluster-based 3D open-frame work indium chalcogenides, [14, 15] with a range of morphologiesalso described, including, thin films [1], and nonmaterial's [16]. There are different technique such as vapor deposition [17], spray pyrolysis [18], Chemical Bath Deposition [19] and evaporation techniques [20] are some of the methods used for the growth of III-VI materials. Out of this chemical bath deposition is simple method used for deposition of indium selenide thin film. There are several challenges regarding the generation of indium selenide in solution. On the one hand, the hydrolyzation of cation ions ofIn(III) is very serious in aqueous solution due to their deficient electron properties, which probably baffles the formation of indium selenides in aqueous solution; on the other hand, indium selenides have complicated stoichiometries including the form so InSe, In2Se3, In4Se3, and In6Se7 [21]. They thermodynamically coexist in a large range of temperatures and often emerge in similar reaction conditions. Moreover, several crystalline phases (a, b, g, d, and k) occur with the same stoichiometry of In2Se3 [22-23]. These electronic and structural features largely restrict the synthesis of pure single phase In2Se3. To the best of our knowledge, the synthesis of pure single phase In2Se3 crystals in solution has not been explored so far. In view of the properties and applications of materials usually determined by their phase structures and morphologies, it is desirable and significant to fabricate pure phase In2Se3 with novel morphology via a solution process. In2Se3 has attracted substantial attention as a promising semiconductor

material for several different applications such as photovoltaic solar cell [24-25] optoelectronics[26] and ionic battery[27] In particular, In2Se3 has been recently used as a programmable material in phase-change random access memory (PRAM).[28-29]

In present work, indium selenide thin films were deposited by chemical bath deposition, using tartaric acid and Na2SeSO3 complex with indium sulfate. The aim of this work is to study the optical, structural, surface morphological and compositional properties of indium selenide thin films using X-ray diffraction, scanning electron microscopy (SEM), electron dispersive Spectroscopy and optical absorption.

II. Experimental Details

The chemicals indium sulphate, selenium powder, hydrazine hydrate and tartaric acid used for the deposition of films were of AR grade. In the present synthesis, solutions of Indium sulphate and selenium powder were prepared in double distilled water respectively in two different beakers, wherein Indium sulphate acts as a precursor of In3+ and selenium powder, that of Se2- as explained in the following steps.

In2Se3 thin films were deposited from acidic bath medium by using chemical bath deposition at room temperature. First, the bath containing 5ml of 0.01M indium sulphate was prepared for In3+ with continuous stirring for 10 minute until a uniform mixture was formed. Second, 1ml of 0.1M tartaric acid, a complexing agent was then prepared in double distilled water through vigorous stirring and added to the first bath containing indium sulphate bath to obtain In3+-tartaric acid complex. Third, 1ml of 80 % hydrazine hydrate was then added to the complex, which helps for obtaining soluble species of In3+ in acidic medium during the reaction. Fourth, a 5ml of 0.1M selenosulfate was introduced in the complex bath under constant stirring of 10 minute. The color of the solution mixture was observed to be changing from colourless to light white, brown and then to dark brown indicating the formation of In2Se3 species. The synthesis process is considered to be based on slow release of In3+ and Se2- ions in bath. The reaction was carried out at room temperature (RT) and sample was taken out after completing the desired reaction time of 46 h.

The structural analysis of the deposited film samples was carried out using X-ray Diffractometer (XRD) (model: Rigaku Dmax -2400, Cu Kα = 0.154 nm) in the 2θ range of 20 to 80°. Scanning Electron Microscope (SEM) (model: JEOL-JSM 6360) was used to study the morphology of chemically deposited In2Se3. UV-Visible spectrophometer (model: JASCO V-670) was used to record optical absorption spectra of the film samples at room temperature in the range of wavelength 300–800 nm.The contact angle measurements were conducted by using contact angle measurement instrument designed and developed in our laboratory.

III. Results And Discussion

3.1 X-ray Diffraction analysis:-

Structural identification of indium selenide thin film was studied with X-ray diffraction technique. XRD pattern, which is not shown, of the chemically deposited films revealed the amorphous nature of In2Se3. Similar arguments have also been reported earlier in literature in case of the In2S3 films deposited on glass and FTO coated glass substrates [10]. However, elemental analysis of the films recorded by EDAX analysis confirms the formation of indium selenide films.

3.2 Morphological analysis:-

The Figure 1(a) (b) shows the SEM images of the chemically deposited In2Se3 films onto the non-conducting and conducting glass substrates at room temperature, respectively. However, from images shown in the figure 1(a) (b), it can be clearly seen that, the rate of the growth of the In2Se3 clusters varies with the substrate. In case of the film deposited on non-conducting soda lime glass substrate the size of the clusters is in the range of 500-600 nm (figure 1 (a)), that of it is about 100-200 nm for the film deposited on conducing glass substrate (ITO). It suggests that, the substrate plays a vital role in controlling the rate of the growth of the clusters in deposition of films with chemical solution technique at room temperature.

3.3 Optical Properties:-

Figure 2 (a) shows the wavelength dependent absorbance spectra of the chemically deposited In2Se3 films showing a red shift for the sample deposited on non-conducting glass substrate. This may be attributed to the large size of the clusters deposited on non-conducting substrate, which is in agreement with the argument made above in the morphological analysis. Optical energy band gap (Eg) of deposited film was determined from their absorption spectra. To determine the optical band gap of deposited indium sulfide thin film plot of (abs)2 vs (hυ) has been plotted and shown in Fig. 2 (b). Spectra shows the energy band gap of about 1.9 eV for the film deposited on glass substrate and that of 1.5 eV estimated for the films deposited on ITO coated glass substrate.

These obtained values are found to be in the agreement with the reported optical band gap values of the indium selenide values varying from 1.2 to 2.0eV with several phases [11-13]. This variation in the band gap values in the present case may be due to the increase in the cluster sizes discussed earlier in the regard of the surface morphology of indium selenide film deposited on different substrate.

IV.   CONCLUSION

In summary, the morphological and optical properties as a function of substrate, reaction time and bath temperature of chemically deposited In2Se3 films were investigated. The study described the evolution of the morphology and optical properties of the deposited films with good correlation among them. The particle size was observed to have increased with prolonged deposition time and have also showed the variation with substrate. This confirms that substrate is also one of the parameter which decides the growth kinetics of the films deposition in chemical bath deposition. The optical absorption properties of the obtained films of In2Se3 have revealed that, these nano systems are suitable for optoelectronic applications including photovoltaics.

V.   Figures
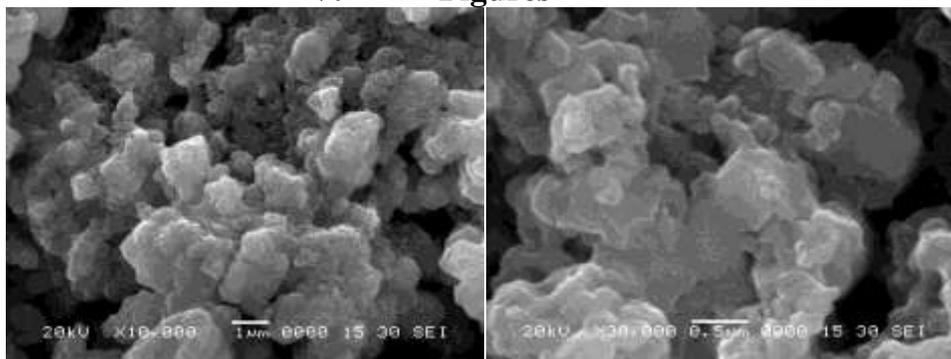
Fig1(a):SEM images of indium selenide thin film deposited onto glass substrates
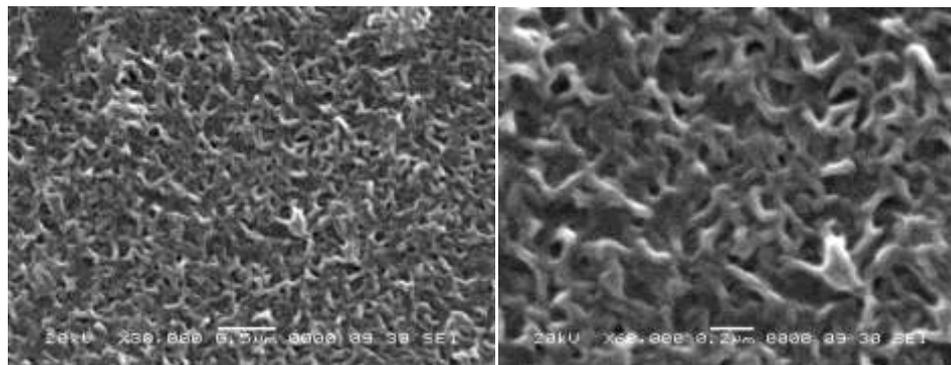
Fig1(b):SEM images of indium sulfide thin film deposited onto ITOsubstrates
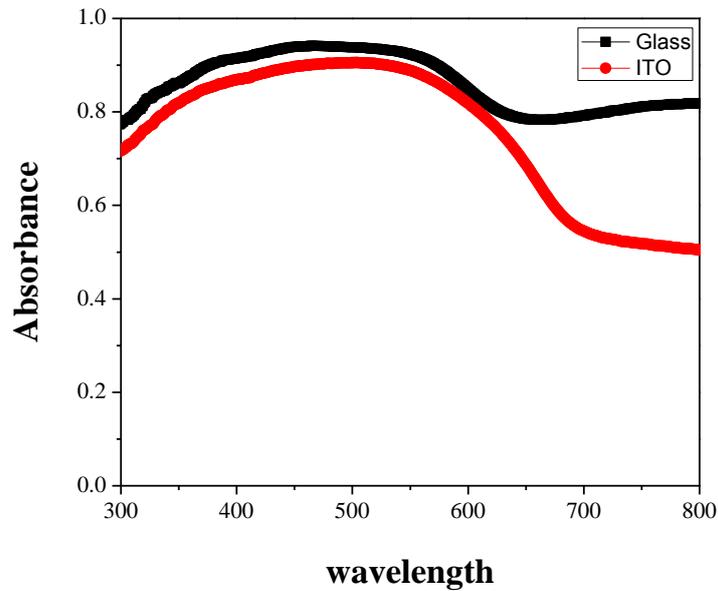
Fig 2(a): Plot of AbsorbanceVsWavelengthfor Indium Selenide films deposited onto glass and ITO coated glass substrates
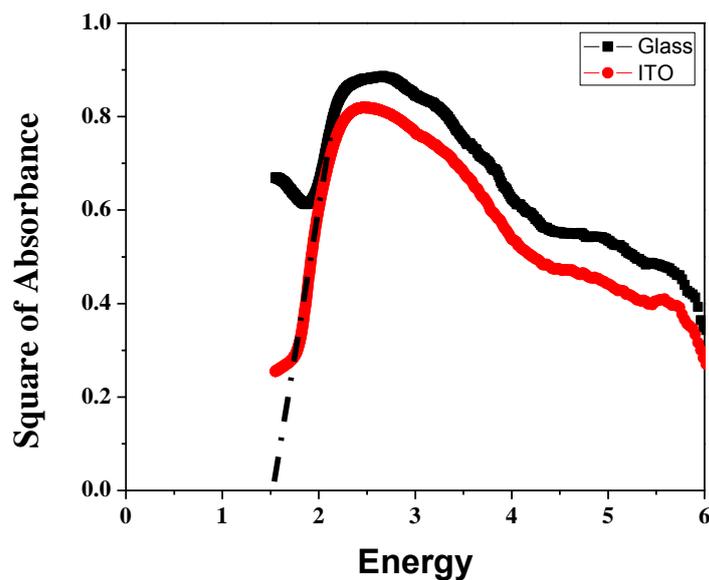
Fig 2(b): Plot of (Absorbance)^2 Vs Energy for Indium Selenide films deposited onto glass and ITO coated glass substrates.

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